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PARTICLE SIZE MEASUREMENT AND THE EFFECT OF PARTICLE SIZE ON THE BURNING TIME OF CHEMICAL DELAY COMPOSITIONS (U)

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U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

PARTICLE SIZE MEASUREMENT AND THE EFFECT OF PARTICLE SIZE ON THE BURNING TIME OF CHEMICAL DELAY COMPOSITIONS

Prepared by:

D. R. Eigsti*
R. D. Dwiggins

Approved by: D. C. HORNIG, Chief
Chemical Engineering Division

ABSTRACT: Since chemical reaction rates in general are proportional to concentration, or surface area, it is mandatory that particle size of fuel-oxidant systems be controlled for optimum burning time performance. Of the many methods of particle size measurement, it must be determined which one is most applicable for control and research use. A literature review was made and samples of powdered metals were analyzed by several methods. These results indicate tentatively that a turbidimetric liquid sedimentation procedure is most suitable.

(*Mr. Eigsti is currently engaged in graduate study at the University of Nebraska. The work reported here was done while Mr. Eigsti was working as a summer employee at the Naval Ordnance Laboratory.)

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U. S. NAVAL ORDNANCE LABORATORY
White Oak, Silver Spring, Maryland

The work reported herein was done under Task RMMO 33 201/212 1/F008 11 001, "Power Sources for Actuated Devices". The information presented represents the combined results of a literature survey and a limited amount of experimental data obtained from various sources. The technical comparison of several commercially available instruments for determining particle size was made with a specific end use in mind. The conclusions are those of the authors and no general endorsement of a specific instrument by the Laboratory is intended or implied. The study will serve as a technical guide for particle size analysis in programs where finely divided powdered materials are used.

W. D. COLEMAN
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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PARTICLE SIZE MEASUREMENT AND THE EFFECT OF PARTICLE SIZE ON THE BURNING TIME OF CHEMICAL DELAY COMPOSITIONS

INTRODUCTION

Chemical delay compositions are fuel-oxidant systems which depend upon a thermochemical reaction for the desired performance. The primary function of this chemical system is to produce heat. Engineering applications are derived from the ability to produce heat at a predictable rate in order to provide the correct time interval between two temperature actuated events.

The chemical reactions in the fuel-oxidant system are governed by the nature and concentration of reactants, their temperature and the pressure in the system. Concentration of reactants in these mixtures must be viewed in terms of intimacy of contact between the fuel and oxidant particles. Fine powders will have a greater amount of surface area and consequently more contact between fuel and oxidant. Thus it is readily apparent that particle size of the reactants will influence the burning time of a given composition. This is shown to a marked degree with tungsten powder which is available in a wide range of particle size distributions. Table I illustrates this effect. Although the percentage compositions are not identical they are close enough that little difference in burning time would be noted if the tungsten fuel had the same surface area The weight average diameter and the surface area were determined on the Micromercograph. It is seen that, under these conditions, a fuel with about twice the surface area will have a linear burning time of about 1/5 of the former.

Obviously, the real factor in the reactivity, or burning rate, of delay compositions is the specific surface area. Average particle diameter, alone, is of less value in predicting reactivity because its correlation to surface area is not always known. However, if an accurate particle size distribution can be determined, surface area can be estimated providing the shape of the particles is known.

In the delay system utilizing manganese fuel and barium chromate-lead chromate oxidants, particle size, or surface area, of the manganese is doubly important because the metal is first treated to stabilize it

TABLE I

Effect of Specific Surface on Burning Time

Fuel Characteristics		Delay Composition					
Type of Tungsten	Surface Area Cm^2/gm	Wt. Ave. Diam. μ	Tungsten %	$BaCrO_4$ %	$KClO_4$ %	Super Floss %	Burning Time sec/in
M-10*	1,377	2.3	40	51.8	4.8	3.4	4.17
ND 3499**	709	4.9	38	52.0	4.8	5.2	21.5

*Samples obtained from Sylvania Electric Products, Inc.
**Samples obtained from Fansteel Corp.

against oxidation after loading. If the particle size distribution is such that the surface area is greater than about 1200 cm^2/gm, the reactivity is too great in the treating process and irregular effects occur in the burning delay column. Manganese fuels having surface areas below about 900 cm^2/gm are too coarse to burn reliably in the D-16 delay compositions. The acceptability of a lot of manganese powder can be checked by its performance when burned under standard test conditions in a composition containing 40% barium chromate, 29.8% lead chromate and 30.2% manganese. An acceptable powder should burn between 12 and 14 seconds per inch in this composition.

DISCUSSION OF PARTICLE SIZE METHODS

General

The numerous methods which have been developed and advocated for particle size analysis indicate the importance and the complexity of the problem. Particle size distribution methods may be classified generally as direct or indirect. Direct methods are those in which particle diameters or volume are determined by measurements on large numbers of individual particles. The microscopic method and the Coulter Counter, which is calibrated to determine the size of a particle from its electrical effect in an electric field, are examples of direct methods. Indirect methods include those which provide for segregation of a mixture of particles, in one way or another, according to their diameters. The quantity of material in selected fractions is then estimated by weighing, by turbidimetric or radiation scattering techniques or by density measurement. Separation of particles into size fractions is usually accomplished by sedimentation in gaseous or liquid media or by elutriation methods. Many texts and treatises are available which adequately described most of these methods. Some of them will be discussed below.

DIRECT METHODS

Microscopic Method

The microscopic method, references (11), (15), (19) and (22), is the most direct one for obtaining particle size. This involves the dispersion of a small sample on a slide and visually sizing the particles. Probably the most important aspect of this method is to get a representative sample

of the material, for only an extremely small amount is needed for each slide. Dispersing the samples may present problems. Several variations are available, ranging from dispersion in a drop of liquid to dry dispersion.

Various eyepieces are available. Some, as in the film micrometer, require direct measurement of each particle, while others have calibrated circles or squares and require comparison or estimation techniques to obtain particle size. For obtaining size distribution, the particles are classified according to size ranges and 200 to 1000 particles must be measured, depending on the statistical accuracy required. Automatic scanning devices have been developed but they require complex photoelectronic equipment.

Because of the lengthy, tedious procedure involved, operator fatigue resulting from repeated counts, and the errors resulting from operator bias in estimation and comparison techniques, the microscopic method is not considered a suitable means for routine particle measurement. The microscope is, however, a valuable instrument for preliminary observation to determine particle shape and agglomeration tendencies.

Coulter Counter

The Coulter Counter, reference (23), is one of the newest instruments for determining particle size distributions. This apparatus is manufactured by the Coulter Electronics Company of Chicago.

The sample is dispersed in a liquid and 1/2 cc of this suspension is forced through a tiny orifice which has an electrode on each side. As a particle passes through the orifice it causes a change in the resistance between the electrodes which is proportional to the size of the particle. This change in resistance produces an electrical pulse which is scaled and counted electronically. To obtain a distribution curve, the pulses are fed to a threshold circuit which records only those above a certain selected magnitude. This gives a point on the distribution curve of percent of particles above the corresponding size. By changing the threshold level, other points on the distribution curve can be obtained. It is reported that data for a 10 point distribution curve can be obtained in 10 minutes. The principle of operation makes it necessary to have a difference in electrical conductivity between the particles and the dispersing medium. A ratio of 3 to 2 or better is necessary. Of course it is essential to have the particles completely deagglomerated.

This method may be suitable for control situations. Data collected in this investigation were insufficient to establish the reliability and precision of the method.

INDIRECT METHODS

General Theory

Sedimentation methods, references (9), (10), (11), (15), (18) and (19), are based on Stokes' Law, which correlates the size of a spherical particle with its terminal velocity of fall in a fluid medium. These methods for particle size analysis depend on the differences in particle velocity created by the dependence of the total settling force on the particle's diameter or size. For a spherical particle settling under the pull of gravity through a viscous medium, the velocity is given by Stokes' Law:

$$V = \frac{2ga^2(d_1 - d_2)}{9\eta}$$

where V = velocity in cm/sec

g = gravitational acceleration, cm/sec^2

a = radius of the sphere

d_1 = density of the sphere, g/cm^3

d_2 = density of the medium g/cm^3

η = viscosity in poises

Thus, it is seen that particles of a given material settling in a given medium will acquire velocities proportional to their diameters. The concentration of particles and the size distribution will vary with time throughout the settling chamber. If the concentration of particles at a given level can be determined at successive time intervals, a size distribution can be calculated. Since most particulate materials with which we are concerned do not have spherical shapes, it is necessary to define a Stokes' equivalent diameter. This is the diameter assigned to an irregular particle, which is equal to the diameter of a spherical particle that has the same density and falls with the same velocity.

In sedimentation procedures, it is essential that the particles be completely deagglomerated and dispersed in the liquid. Agglomeration is a result of several factors, and probably the most important is due to the attraction particles have for each other as a result of small electrical forces. Particles having diameters below about 2 microns are most susceptible to this effect.

Once the proper dispersing medium is chosen, it is necessary to find the most effective dispersing agent and technique for obtaining complete deagglomeration. The technique should provide the initial force for deagglomeration, and the dispersing agent should prevent reagglomeration and flocculation once the particles are in the suspending medium.

Another point is that very fine particles settle slowly, thus lengthening experimental time. This is a disadvantage of most liquid sedimentation methods.

It should be kept in mind that in all sedimentation methods it is assumed that the particles fall freely, with no interruption. Stokes' Law deals with a single falling sphere. Thus, anything which interferes with the sedimentation process will be a source of error. If the initial concentration is too large the falling particles will interfere with each other. Tests have shown that if a concentration of one volume percent or less is used, the interference between particles is negligible, reference (9).

The following methods describe some of the various procedures for obtaining the data on particle concentrations during the sedimentation process.

Diver Method

In this method, references (9), (10) and (15), the specific gravity at a point in the suspension is determined by small scaled bulbs called divers. A series of bulbs of decreasing specific gravity is used. A diver is released at the surface of the suspension and its distance below the surface is measured at the end of a selected time interval. Using Stokes' Law, the diameter of a particle which falls this distance in the elapsed time may be calculated. Knowing the specific gravity of the diver, the initial suspension, and the suspending medium, permits calculation of the percentage of particles finer than that size. Each diver gives information for only one percentage finer than fraction, thus the whole series must be used to obtain a size distribution curve.

The disadvantages of this method are readily evident. A large concentration is necessary, thus particle interference and agglomerations may be present. Since the divers are placed directly in the suspension, they may interfere with the settling process. If very fine particles are present, the experimental time will be prohibitively long.

Due to the inherent inaccuracies, and the length of time involved in obtaining the necessary data this method is considered to be generally undesirable for either control or laboratory determinations.

Hydrometer Method

The hydrometer method, references (9), (10), and (17), is similar to the diver method in that it measures the specific gravity of the suspension at various levels below the surface. A hydrometer is used, and it is withdrawn after each measurement. The center of the bulb is the point of concern, so the stem must be calibrated to show the depth of this center below the surface. Several corrections need to be applied to obtain a true reading. For instance, a correction is necessary to account for the rise in liquid level due to the insertion of the hydrometer. Specific gravity and depth reading are taken at predetermined times, and calculations are similar to those of the diver method.

In general, this method is also considered to be undesirable for control or laboratory determinations since the same disadvantages which exist in the diver method are present.

Pipette Method

This is probably the most common of the increment sedimentation methods, references (7), (10) and (15). Samples of the suspension are withdrawnat predetermined settling times at a fixed level. The concentration of each sample is determined by evaporation to dryness and weighing. A plot is made of C/C_o versus time, where C is the concentration in weight percent. Slopes of this curve are taken, and with diameters calculated from Stokes' Law, a size distribution curve is determined.

A new pipette with sampling tubes at three different levels has been developed. This reduces the time necessary for a determination when very fine particles are present.

As in the two previous methods, a high concentration is necessary, thus the problems of interference and agglomeration are present. Tests have shown that the results vary with the size of the sampling tube, the position of the orifice at the tube end, and the speed of withdrawing the sample, reference (10). It is necessary to assume that all of the sample comes from the same level as the orifice. This may or may not be true. Withdrawing the sample itself may interfere with the settling process.

In view of these inaccuracies and sources of variation, this method is considered undesirable for control or laboratory particle size distribution determinations.

Sedimentation Balance

The sedimentation balance continually weighs the accumulation of particles that have settled out of the suspension. Various methods are available for following the settling process. An automatic recording device may be used, or a lever arm arrangement with a pointer and scale is also adaptable. Weight readings are expressed as percentages of the total accumulated weight, and plotted against the natural logarithm of time. This curve is differentiated and these values plotted on the same graph. The difference between the two curves gives the weight percent of particles greater than the size which corresponds to the time of fall as given by Stokes' Law. Repeated calculations yield a distribution curve.

Several serious disadvantages are present. It is rather difficult to disperse the sample completely and then introduce it into the sedimentation medium above the pan. Due to the fact that the pan moves downward during the settling process the depth of fall gradually increases; this action, along with the density changes which occur in the suspension, causes convection currents in the dispersing medium, thus introducing errors. A high concentration is necessary, so interference and agglomeration may be present. The slow fall of fine particles is also a disadvantage and differentiating the curve reduces the accuracy.

A variation of the cumulative weight technique, references (15) and (23), uses a gas rather than a liquid for the sedimentation medium. Any method using a gaseous medium would seem to be preferable to one using a liquid sedimentation medium. The reason is that particles settle much faster in a gas, thus allowing use of a longer sedimentation column which should give greater accuracy.

An instrument which is readily available is the Micromerograph manufactured by the Sharples Corporation of Philadelphia. A small sample is forced through a conical shaped deagglomeration slit with compressed nitrogen gas. The sample then enters an eight foot sedimentation column filled with air. The particles settle out onto the pan of a servo-electronic balance which automatically records the accumulated weight versus time. This accumulated weight-time curve is interpreted by using two templates which are based on experimental calibrations and are reported to take into account discrepancies arising due to non-sphericity of the particles and variations in initial velocity.

An inherent disadvantage of the Micromerograph is the effect of static charges on the particles, despite the fact that anti-static agents and devices are used. This is largely responsible for the significant loss of fines in the 0-5 μ range, which has been reported in reference (24). The reported loss of fines has been confirmed on the Micromerograph which is in operation at this laboratory. The "hang-up" usually ranges from 30 to 70% of the original sample. It is this effect which renders the performance of the Micromerograph something less than satisfactory. Several corrective suggestions have been proposed. These mainly involve treatment of the particles or the instrument with anti-static solutions or devices. Nocke and McLean, reference (14), have been able to eliminate the reagglomeration tendencies of the particles by ionizing the air at the deagglomerator exit, with an X-ray beam. However, the effect on the hang-up was not mentioned. To date, the problem of "hang-up" remains unsolved.

It is felt that the Micromerograph would be a suitable instrument for control analyses if some reliable means for overcoming the "hang-up" effect could be found.

Pressure Method

This method, reference (4), makes use of the density change which occurs as the particles settle out of the suspension. A settling tube is fitted with a capillary side arm which serves as an inclined manometer. The side arm is filled with clear suspending medium, the settling tube being filled with the suspension. As the particles settle out, the density decreases at any given point, thus the meniscus in the inclined manometer begins to recede. Meniscus positions are recorded at various times and these are expressed as fractions of the total recession. This data is plotted and tangents are drawn to the curve and extended till they intercept the axis. The difference between any two of these intercepts will be the weight percent of the total sample corresponding to the size range which is calculated from Stokes' Law by using settling times given by the two tangents.

This method has several sources of error. As in the previous methods, the high concentration required introduces problems of particle interference and agglomeration. As the meniscus recedes, some of the clear liquid from the side arm will flow into the settling tube and cause convection currents which will interfere with the settling process.

Centrifugal Method

When extremely fine particles are present in a sample they will settle slowly under ordinary gravitational force. In order to reduce the time necessary for a determination, centrifugal force may be used to assist the settling process, references (8), (10) and (15). It should be kept in mind that the centrifugal device only assists the settling, therefore it must be used in conjunction with some method of actually determining the particle size.

Johnson, reference (10), investigated centrifugation in an attempt to explain differences found in experimental data. He made the hypothesis that these differences were due to the fact that larger, faster falling particles give an impetus to the smaller, slower falling ones. This effect would definitely be present if a sample with a fairly wide size range were being analyzed by centrifugal methods.

Elutriation Method

Elutriation methods, references (15), (16), (17), and (19), actually fractionate the powdered sample into several size fractions by a vertically moving column of fluid. A commercially available instrument is the Roller Analyzer which uses air as the fractionating medium.

The sample is held in a U-tube which is constantly agitated to assure air contact with the whole sample. The air is passed through the U-tube and a vertical column at a known velocity, and only those particles which have a terminal velocity of fall less than the velocity of the moving air are carried over and separated. By varying the air velocity and the diameter of elutriator tube, various size fractions can be separated.

Several major disadvantages are present. At lower velocities the air flow through the elutriator is streamline, which means that the velocity gradient across the tube diameter is parabolic. The maximum, at the center of the tube, is twice the average velocity. Because of this wide range of

velocities through the tube, a sharp separation is not possible. Also, the instrument separates the sample into fractions, and each fraction would need to be analyzed by some other method to determine its actual size distribution. If 10% of the particles are less than 5μ in diameter, a complete fractionation would require about 8 hours, reference (3). This would be prohibitively long.

This method is not considered suitable for control or laboratory determinations due to the length of time involved and the inherent inaccuracies present.

Turbidimetric Method

Turbidimetric methods for particle size analysis are used in conjunction with sedimentation procedures to determine the concentration of particles at given distances below the surface at successive time intervals. From this data, and Stokes' Law, particle size distribution of the sample can be calculated.

When a beam of light is intercepted by a turbid medium, part of the incident light is absorbed, part is directly reflected and part is scattered. The attenuation produced is a function of the concentration, particle size distribution and color of the suspension. If a beam of monochromatic light of intensity I passes through a lamina of thickness dl, the intensity will be reduced by scattering by an amount proportional to I and the thickness dl. Then the decrease in intensity

$$dI = - bI\,dl \qquad (1)$$

where b = is termed the scattering coefficient. Similarly, for absorption, alone:

$$dI = - k\,I\,dl \qquad (2)$$

where k = the absorption coefficient.

Integrating the above equations, we obtain,

$$\int_{I_0}^{I_t} \frac{dI}{I} = -b \int_0^l dl \qquad (3)$$

or

$$\ln \frac{I_t}{I_0} = - bl \qquad (4)$$

and

$$\int_{I_0}^{I_t} \frac{dI}{I} = -k \int_0^l dl \qquad (5) \quad \text{or,} \quad \ln \frac{I_t}{I_0} = -kl \qquad (6)$$

Solving for I_t and combining equations (4) and (6),

$$I_t = I_0 e^{-(b+k)l} \qquad (7)$$

The expression (b + k) is called the extinction coefficient and is given the symbol σ. Then

$$I_t = I_0 e^{-\sigma l} \qquad (8)$$

If light attenuation is due mainly to scattering, which is usually the case in turbidimetry, equation (4) may be written

$$\frac{I_t}{I_0} = e^{-(K\pi r^2 nl)} \qquad (9)$$

where n = number of particles per unit volume of dispersion

K = total scattering coefficient = the effective scattering cross section divided by the geometric cross section

πr^2 = cross section area of particle

Values of K have been tabulated for particles of various diameters. For extremely small particles K is nearly zero. Its value increases rapidly to between 3 and 5 for particles in the range of approximately 0.3 to 0.7 microns. As the size of the particle increases, K drops to a constant value of 2. When values of K are known, and when either the particle diameter or the number of particles are known, the other may be determined from the ratio $\frac{I_t}{I_0}$. If both n and r are unknown they may be determined by making transmission measurements at two different wave lengths and setting up simultaneous equations using equation (9).

Through a combination of sedimentation and transmission measurement, a particle size distribution can be found. Tranquil settling of a dispersion of non-uniform particles will result in a separation of particles according to size so that transmission measurements at known distances below the surface at selected time intervals, will, with Stokes' Law, give the concentration of particles of known diameter. Thus a size frequency distribution can be obtained.

Wagner, reference (21), presented a method for particle size determination which led to the development of the Wagner Photoelectric Turbidimeter. This apparatus has the optical system on a rack which can be moved vertically to examine the suspension at different levels. Musgrave and Harner, reference (13), used a variation of Wagner's original method in which the light beam traverses the suspension at a fixed distance below the surface. A plot is made of percent light attenuated versus time. From this, increments of light attenuation for various size ranges are determined. These values are converted to weight percent by the use of "equivalent hiding power"factors.

The usual problems encountered with any sedimentation procedure are present. It is necessary to use a dispersing liquid compatible with the materials being tested. Also, dispersing agents and technique must ensure complete dispersion and prevent agglomeration. These factors may vary with materials and therefore require special attention when new materials are to be analyzed.

With most materials the above problems can be solved satisfactorily and the turbidimetric method offers a convenient and fairly rapid method for control or laboratory use. A small concentration is sufficient so that particle interference and re-agglomeration tendencies are negligible, in contrast to other sedimentation methods which require larger samples. The settling process is followed without any instrument interference during the run. The method also allows a decrease in the time for an analysis when very fine particles are present because the sedimentation chamber can be lowered thus avoiding a long waiting period for the fine particles to drop into the light path.

EXPERIMENTAL WORK

The turbidimetric method appeared to be one which might offer improved accuracy and less time per determination. In order to better evaluate this method, experimental work was done by one of the authors

on an Eagle-Picher Turbimeter at Diamond Ordnance Fuze Laboratories. Runs were made on four lots of tungsten.

At least two samples from each lot were analyzed. The experimental procedure followed was similar to that given in reference (14).

Experimental work was also done on a light microscope. Two samples from one lot of tungsten were analyzed in order to determine if any correlation existed between this and other methods of particle size analysis. Three slides were made up from each of the samples. A total of 300 to 400 particles per sample were sized, using all 3 slides of that sample. The eyepiece was divided into 23μ squares, the center one of which was subdivided into 4.6μ squares. The particles were sized by estimating their Martins' diameter, reference (7), and then they were tabulated in size ranges.

Prior to the beginning of this work, samples from two lots of tungsten were sent to Coulter Electronics, for analysis on a Coulter Counter, and to the National Bureau of Standards for analysis by the B.E.T. nitrogen adsorption method. These results were then compared with those obtained from the Turbimeter and from the Micromerograph which is in operation at this Laboratory.

In sedimentation methods, it is generally assumed that the particles are spherical. Continuing this assumption, the total surface area may be calculated from the particle size distribution curve. If it is assumed that this curve is a true representation of the facts, the most reliable value for surface area will be obtained by summation of the areas for the largest number of weight fractions or, in other words, the smallest increments of particle diameter. However, due to assumptions and normal experimental variables which introduce some uncertainty into the curve, calculation of surface area with numerous fractional ranges corresponding to small increments of particle diameter is not usually justifiable. As a compromise, division of the sub-sieve range into diameter intervals in the form of a geometric progression will usually provide a resonable estimate of the surface area.

The relationship between surface area per gram and diameter gives the following:

$$S = \frac{\pi D^2}{W}, \text{ where } W = \text{weight}$$

since W is derived from the density of the material, G,

$$G = \frac{W}{V}, \text{ or } W = G \times V$$

$$\text{then } S = \frac{\pi D^2}{VG} = \frac{\pi D^2}{\frac{\pi D^3 G}{6}} = \frac{6}{DG}$$

$$\text{or } S = \frac{6 \times 10^4}{DG}$$

where $S = cm^2/gm$

D = diameter in microns

G = density of the material in grams per cubic centimeter

From this equation, surface area for any given diameter particle can be found and if this is multiplied by the weight fraction of sample having that diameter, a figure is obtained for the total surface area of particles of this diameter in the sample. Summation of these values for the various diameters gives the total surface area for the powder. This can be expressed by an equation of the following type:

$$\text{Total Specific Surface} = \frac{6 \times 10^4 (W_2 - W_1)}{D_A G} + \frac{6 \times 10^4 (W_4 - W_2)}{D_B G}$$

$$+ \frac{6 \times 10^4 (W_8 - W_4)}{D_C G}$$

where W_x = weight fraction of particles less than diameter x

$D_{A, B, C}$ = average particle diameters in microns over the interval.

In the above way, the following equation was developed to give the specific surface of tungsten powders in cm^2/gm,

$$S = 1040W_2 + 520W_4 + 260W_8 + 130W_{16} + 65W_{32} + 65W_{64}$$

The values of W can be taken from the particle size distribution curve. The equation applies only to tungsten or materials of equal density.

RESULTS

The results of this project are partially summarized in Table II. Column 6 lists the burning times of standard delay test mixtures. Since the tests were carried out at identical conditions of percentage composition and temperature, and in the standard test fixture described in NAVORD OS 11131, these burning times serve as a means of checking the relative fineness of the powdered fuels. The rapid burning times indicate that both M-10 and M-20 are very fine. Also, the M-10 is definitely finer than M-20, as shown by the difference in their burning times.

Keeping in mind that the specific surface is a gauge of the fineness of a powder, comparison of the result for M-10 and M-20 in Table II shows that the Turbimeter yielded analyses which were consistent with the burning time data, that is, M-10 is a finer powder than M-20. The Micromerograph showed a smaller difference between these two lots. The Coulter Counter gave results which were inconsistent with the burning times. It showed both powders to be quite coarse, as indicated by the small surface area, and that of the two, M-20 is finer. The B.E.T. nitrogen adsorption method also indicated coarse powders, and failed to show any difference between the two lots.

Two lots of another type of tungsten were run on the Turbimeter and Micromerograph as a further test of these instruments. Delay compositions were also made up using powders ND 3499 and ND 3657. Since the burning times for compositions burning in the 40 second range may vary by as much as 3-5 seconds from batch to batch, the difference in burning time for these two compositions cannot be significantly related to the difference in particle size. However, the differences in burning time between these coarse powders and the finer M-10 and M-20 is readily apparent.

A comparison of the distribution curves given by the Turbimeter, Micromerograph and Coulter Counter for identical samples of tungsten is shown in Figure 1. It seems possible that the lack of fines shown by the Micromerograph was due to the excessive hang-up which has been reported. The extreme coarseness of the results given by the Coulter Counter is unexplainable, however, inadequate deagglomeration could produce this effect.

The time required to determine a complete size distribution curve on the Turbimeter and the Micromerograph varies with the fineness of the particulate material. In this experimental work, the longest time involved in obtaining a size distribution curve on the Turbimeter was about 2 hours 30 minutes. The time for analyzing a comparable powder on the Micromerograph

TABLE II

Comparison of Results From Four Particle Size Methods

Tungsten Sample Lots	Turbimeter Wgt. Ave. Diameter μ	Turbimeter Specific Surface cm^2/gm	Micromerograph Wgt. Ave. Diameter μ	Micromerograph Specific Surface cm^2/gm	Coulter Counter Wgt. Ave. Diameter μ	Coulter Counter Specific Surface cm^2/gm	B.E.T. Specific Surface cm^2/gm	Burning Time sec/in.
M-10*	1.5	1,295	2.3	1,377	11.8	781	1,000	3.41
M-20*	3.1	1,107	2.5	1,227	11.5	817	1,000	4.62
ND 3499**	5.4	688	4.9	709				42.04
ND 3657**	6.5	553	5.0	674				44.96

*Samples obtained from Sylvania Electric Products, Inc.
**Samples obtained from Fansteel Corp.

at this Laboratory was about 5 hours. It should be kept in mind that about 4 hours of this was necessary to allow the sample to settle. Since the recorder is automatic, the operator was free to do other work during this time. Also it is possible to adapt a recorder to the Turbimeter, and thus free the operator of a similar proportion of the experimental time.

The precision of the Turbimeter is reported to be $\pm$ 2%, reference (12). Table III shows the precision obtained in this work. Column 4 is the standard deviation of the specific surface values, and column 5 gives these as percentages of the mean specific surface values.

An indication of the reproducibility of the Turbimeter is shown in Figure 2.

The results of the microscopic particle size determination are shown in Figure 3. The number-size distribution of a sample was converted to a weight-size distribution using a method given by Herdan, reference (7c). This was compared with the weight-size distribution given by the Turbimeter and the Micromerograph for the same material. As seen in Figure 3, which is a log-probability plot, there seems to be no correlation.

It is felt that this is partially due to the effect of the extremely small samples which are used in the microscopic method. This presents problems of obtaining a representative sample and complete deagglomeration.

CONCLUSIONS AND RECOMMENDATION

A perusual of the results indicates that, among the methods considered for particle size analysis, the turbidimetric method as exemplified by the Eagle-Picher Turbimeter appears to most nearly conform to the acceptable criteria discussed throughout this report. The precision and reliability seem to be adequate. Also, the simple technique involved and the time necessary to complete an analysis make the Turbimeter readily adaptable to production situations.

Although finely divided metals were the only powders analyzed on the Turbimeter during this study, the instrument is adaptable to a wide variety of particulate materials, including both organics and inorganics.

There are certain materials which are not adaptable to this method, reference (13). These are very low specific gravity materials as flour,

TABLE III

Precision of Eagle-Picher Turbimeter Experimental Work

Tungsten Lot	Sample No.	Specific Surface cm^2/gm	Standard Deviation cm^2/gm	Percent of Mean
M-10*	2	1,802	13.6	0.76
	3	1,789		
M-20*	4	1,056		
	5	1,171	58.7	5.3
	6	1,093		
ND 3499**	13	694	9.2	1.3
	16	681		
ND 3657**	14	558	7.1	1.3
	15	548		

*Samples obtained from Sylvania Products, Inc.
**Samples obtained from Fansteel Corp.

extremely fine, dark colored pigments such as Prussian Blue, and materials with no particles above 0.5μ radius.

The Micromerograph also gave surface area values which were consistent qualitatively, with measured burning times. However, its accuracy is adversely affected when the powder being measured contains a high percentage of fines. Consequently, it appears that the liquid sedimentation-turbidimetric method has fewer drawbacks and would seem, at this time, to be the most suitable one for general particle size distribution measurement.

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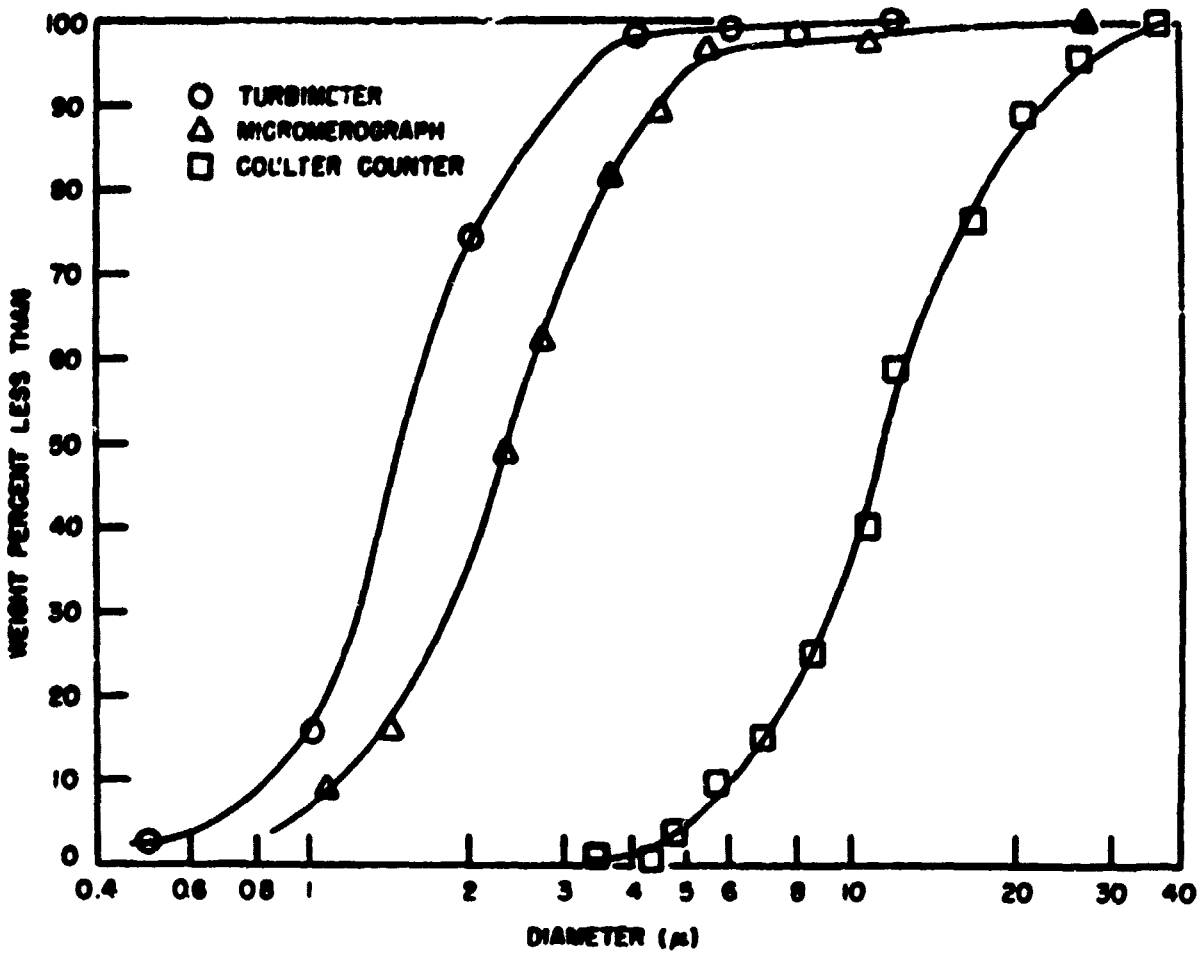

FIG. 1 SIZE DISTRIBUTION CURVES FOR THREE METHODS OF PARTICLE SIZE ANALYSIS

TUNGSTEN M-10

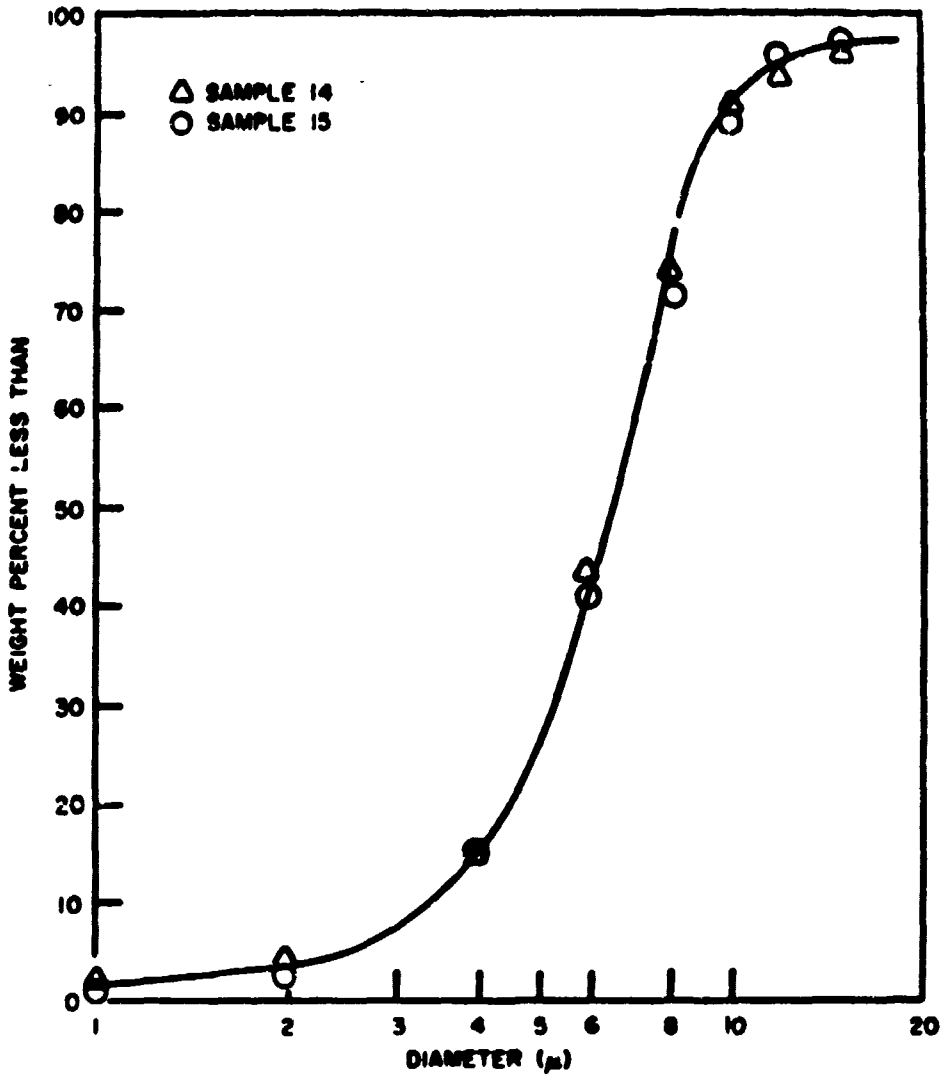

FIG. 2 REPRODUCIBILITY OF TURBIMETER

TUNGSTEN ND 3657

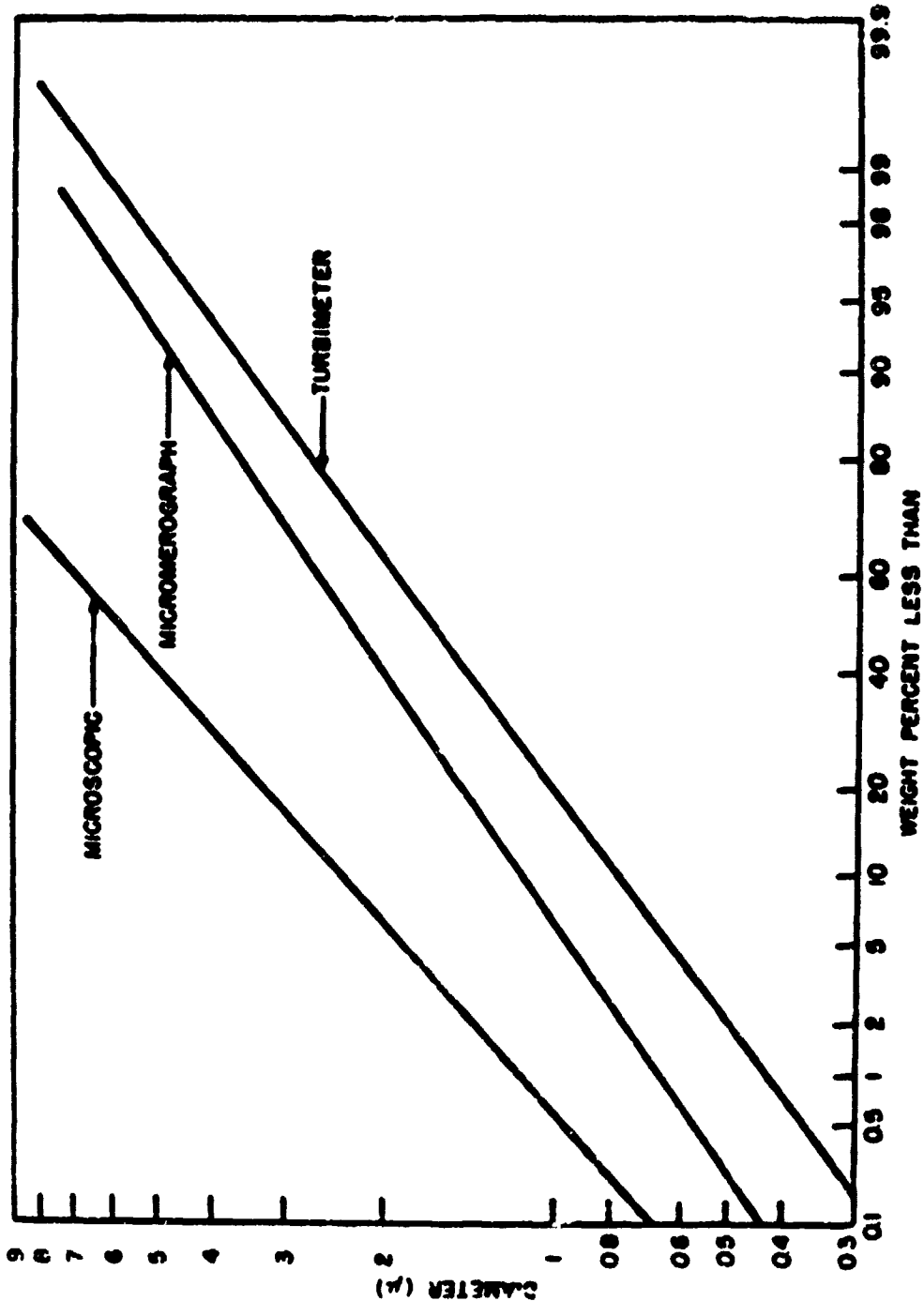

FIG. 3 COMPARISON OF MICROSCOPIC METHOD OF PARTICLE SIZE ANALYSIS

TUNGSTEN M-10